PROCEEDINGS

THE EFFECTS OF TEMPERATURE ON PHOSPHORES–CENCE AND FLUORESCENCE.[1]

By EDWARD L. NICHOLS.

(*Read April 22, 1910.*)

Fluorescence and phosphorescence are closely connected phenomena, the precise relation of which is not completely settled. In a general way we may say that the emission of light by a body under any one of the numerous stimuli which produce luminescence when observed during excitation is termed fluorescence; the after glow is phosphorescence. According to the quite generally accepted view, first expressed by Wiedemann and Schmidt[2] and since developed by Merritt[3] and in somewhat different form by Lenard[4] and others, luminescence is a phenomenon of dissociation in which negative ions or in the language of Lenard " electrons " are separated from the molecules by the action of light, cathode rays, X-rays, the radiation from radioactive materials, etc. These are supposed to return later to the aggregation from which they have been torn loose or to some other molecule and to produce by their collision the vibrations which are the source of the emitted light.

The formation of these free ions is a gradual process ; measured in terms of the time of vibration of light, indeed, it is almost infinitely slow.   If the fluorescence of a body subjected to moderate illumination be measured from second to second it will be found to increase in brightness, first rapidly, then, more and more slowly ; approaching a maximum in some cases only after several minutes.

From such observations a sort of saturation curve may be plotted. In Fig. 1, which is from measurements by Professor Merritt and the present writer,[5] curve A is such a saturation curve
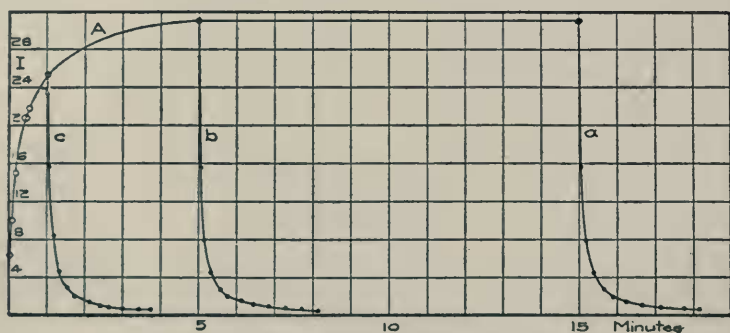

Fig. 1.   Curves of saturation and of decay.

obtained by observing the increase in the brightness of fluorescence of a specimen of Sidot blende during an interval of fifteen minutes. Immediately upon the cessation of excitation the light from the fluorescent body begins to decrease ; first rapidly, then more and more slowly and this phase of the phenomenon which may likewise be expressed by a curve, called the " curve of decay " is called phosphorescence.   Curves a, b and c in Fig. 1 are the curves of decay of the phosphorescence of this specimen of Sidot blende when excitations is ended after 15 min., 5 min., and 1 min. respectively.   The law of decay is always the same although the length of time required for the afterglow to become so feeble as to be invisible may vary from many hours[6] to an immeasurably small fraction of a second.

[5] Nichols and Merritt, *Physical Review,* Vol. XXIII., p. 46.
[6] Surfaces coated with the ordinary phosphorescent zinc sulphide or Balmain's Paint if exposed to sunlight and taken into a dark room have been know to continue to glow for months with sufficient intensity to fog photographic plates.

In the case of fluorescent liquids it was found by one of my former pupils, Dr. Waggoner,[7] that even with a special form of phosphoroscope, by means of which observation less than a thousandth of a second after the cessation of intense illumination were possible, no phosphorescence could be detected. It should be remembered, however, that 1/10,000 or even 1/1,000,000 of a second is a very long time measured in terms of the frequency of light, since the particles of a phosphorescent body emitting green light would oscillate some 500,000,000 times in a millionth of a second. We are not in position therefore to say that fluorescent liquids, in none of which phosphorescence has been observed, differ from phosphorescent bodies save in the rapidity with which the light decays.

By the use of this instrument Dr. Waggoner was likewise able to trace the phosphorescence of various compounds back to its very source at the cessation of excitation and to show how in the cases which he studied fluorescence merged into phosphorescence without discontinuity and the quality, or distribution of wave-lengths in any single band in the spectrum remained unchanged during the first few thousandths of a second. Professor Merritt and the present writer[8] had previously shown that in the case of a substance of slow decay (Sidot blende) the phosphorescence spectrum is identical, so far as the single band under observation was concerned, with the fluorescence spectrum and that " if any change occurs in the form of the phosphorescence spectrum during decadence, this change is extremely small."

According to this view the relation of phosphorescence to fluorescence would seem a very simple one but more detailed study develops complications such that the complete theory of the subject is as yet far from being perfected. Some of these complications are brought out particularly when we subject fluorescent or phosphorescent substances to change of temperature and it is with some of the phenomena accompanying such changes that I propose to deal in the present paper.

[7] Waggoner, *Physical Review,* Vol. XXVII., p. 209, 1908.
[8] Nichols and Merritt, *Physical Review,* Vol. XXI., p. 257, 1905.

When a body capable of phosphorescence is either heated or cooled and then exposed to light the intensity of its fluorescence is found to vary as are also the intensity and duration of its phosphorescence. Mere observations with the unaided eye suffice to show the following:

1. Very great changes occur in the rate of decay as the result of either cooling or heating.

2. The color of phosphorescence frequently differs at different temperatures.

3. The color of phosphorescence may be seen to vary markedly during decay, one tint gradually merging into another.
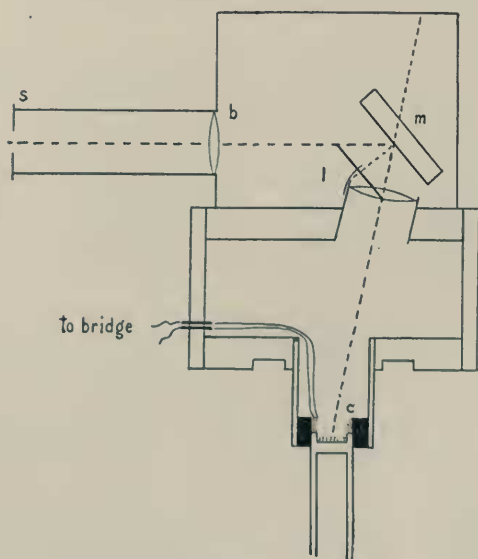

Fig. 2.   Apparatus for cooling.

4. Fluorescence of one color is often followed by phosphorescence of another. W. S. Andrews,[9] for example, has noted the following in the case of artificial phosphorescent substances.

Compounds containing.	Fluorescence.	Phosphorescence.
(a) Zinc and manganese.	light pink	deep red
(b) Cadmium, manganese and sodium.	light pink	orange-yellow
(c) Cadmium and manganese.	yellow	light green

[9] Andrews, W. S., *Science*, Vol. XIX., p. 435, 1904.

To determine more exactly the effects of temperature on the duration of phosphorescence the following experiments, in which Mr. J. F. Putnam assisted me, were made. Several sulphides of known composition of the sort prepared by the method of Lenard and Klatt, a number of which are now on the market, were cooled by means of liquid air. The form of apparatus used is shown in Fig. 2.

The source of light was a flaming arc between carbons which were filled with salts yielding an ultra-violet spectrum of great intensity and unusual range. These carbons are known commercially as the "brilliant white." They gave an arc which under the conditions of our experiments excited the substances under observation to complete saturation in about six seconds.

The lamp was of the vertical carbon type with a large upper carbon, cored but not impregnated, and a smaller impregnated carbon below. The direction of the current was such as to make the latter the positive terminal. Such a lamp burns several minutes without feeding with an arc from one to two centimeters in length and of sufficient steadiness for the purpose in question.

A condensing lens of quartz 20 cm. focal length and 5 cm. diameter threw an image of the arc upon the wide horizontal slit s, the edges of which excluded light from both carbon tips. The light after passing the slit was rendered parallel by the quartz lens l' and fell upon a plane mirror m of speculum metal by which the beam was reflected obliquely downwards at an angle of about 70° through the similar lens l'' which caused an image of the slit upon the substance to be observed. The substance in a thin layer of powder was contained in a shallow capsule at the top of a bronze tube about 20 cm. long. When in position the top of this tube was surrounded by a massive collar of copper which in turn was supported by a tube of hard fiber which afforded excellent thermal insulation. The whole was boxed in to prevent the gathering of frost. Observations of the phosphorescent substance were made through a horizontal tube inserted in the side of the box above the capsule and having a rectangular prism p at the inner end, as shown in Fig. 3.

To cool the phosphorescent compound the lower end of the bronze tube was submerged in a cylindrical Dewar flask containing liquid air and by the vertical adjustment of this tube any temperature from that of the room to about — 185° could be reached and
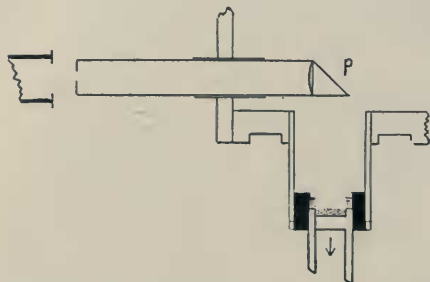

FIG. 3   Device for observing the cooled substance.

maintained.   The temperatures were measured by noting the electrical resistance of a previously calibrated coil of fine copper wire C (Fig. 2) imbedded in the copper cylinder and immediately surrounding and in contact with the capsule.   A shutter, the opening
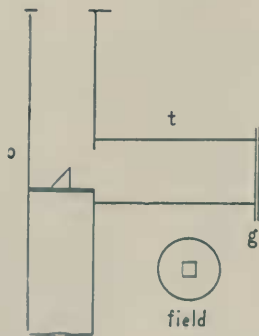

FIG. 4.   The photometer.

and closing of which was automatically recorded by a chronograph, was used in making exposures to excitation.

For the determination of the curves of decay a specially designed photometer was used.   This consisted of a slight tube O, Fig. 4, mounted horizontally in front of and coaxially with the

observing tube in the side of the box already described. Within
this sight tube and in the focus of the eyepiece e a disk of thin
plane glass was mounted in the middle of which was fastened, with
Canada balsam, a very small rectangular prism. Opposite this a
a side tube t was inserted, the outer end of which was covered
with a screen of ground glass g. When the screen was illuminated
from without an observer at the eyepiece saw a rectangular patch of
light—the face of the reflecting prism—surrounded by the field of
light due to the phosphorescent surface. The brightness of this
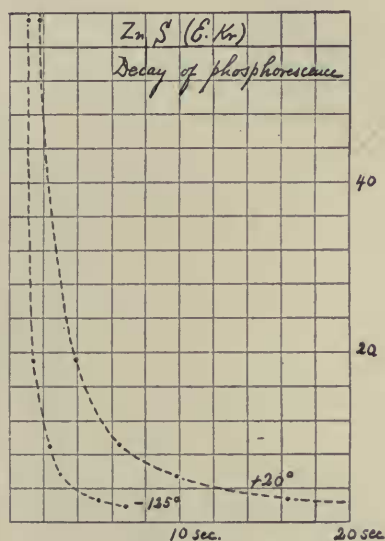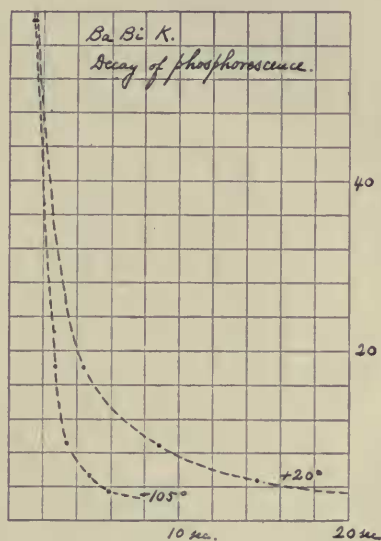

FIG. 5.   FIG. 6.

patch was varied, in making measurements, by the movement of a
small frosted tungsten lamp (boxed in and viewed through a small
aperture) which travelled along a photometer bar in the direction
of the axis of the side tube.

To determine the curve of decay with this apparatus the com-
parison lamp was set at a selected point on the photometer bar, the
shutter was opened for ten seconds to secure saturated exposure of
the specimen under observation, and at the instant when the decay-
ing phosphorescence had fallen to the degree of intensity which

balanced the light of the comparison lamp as determined from the appearance of the contrast field of the photometer, a record was made on the same chronograph sheet on which the closing of the shutter had been automatically registered.

This procedure was repeated with the comparison lamp at various positions on the bar. Typical results obtained in this way are
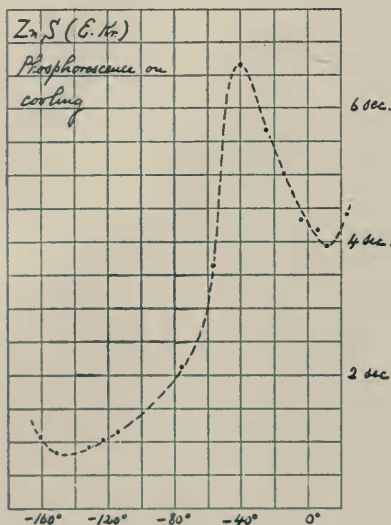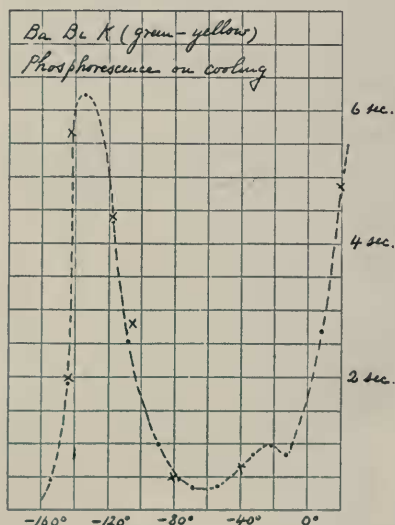

FIG. 7.

FIG. 8.

given in Figs. 5 and 6. Fig. 5 shows the curves of decay of phosphorescence in a sample of ZnS at $+20°$ and at $-125°$. In Fig. 6 similar in curves for a phosphorescent barium sulphide prepared by the method of Lenard and Klatt and having as its active metals bismuth and potassium are given for $+20°$ and $-105°$.

The more rapid decay exhibited by both of these substances at the low temperatures does not necessarily indicate lower initial intensity of phosphorescence. Indeed in the case of the Ba Bi K compound the initial intensity at $-105°$ which may be estimated from the decay curves by plotting these in the manner already described by Professor Merritt and myself[10] in which the reciprocal of the square root of the intensity is taken as ordinates is several times higher than the intensity at $+20°$.

[10] Nichols and Merritt, *Physical Review*, Vol. XXII., p. 280, 1906.

So marked are the fluctuations in the duration of phosphor-escence in these substances on cooling that at many temperatures the effect dies down more rapidly than it can be followed with the apparatus just described. It is, however, possible to secure an almost complete record of the fluctuations of phosphorescence with temperature by allowing the substance to cool slowly throughout the entire range of temperatures. The photometer carriage is set at a convenient distance and records made of the times required for the phosphorescence to attain this intensity at the various temperatures
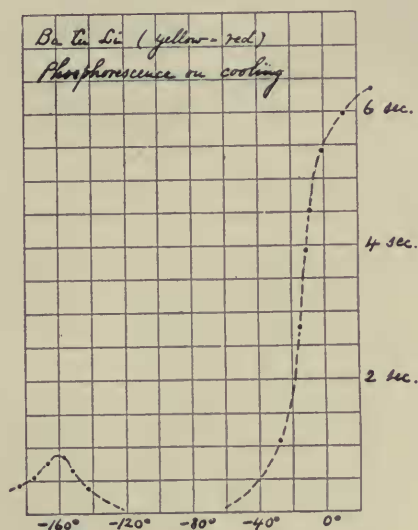

FIG. 9.

through which the substance passes in cooling. Measurements of this sort were made by Mr. Putnam and myself in the case of a number of phosphorescent sulphides. Three characteristic cases are shown in the curves in Figs. 7, 8 and 9. Two of these sub-stances are those for which the decay curves have been given in the previous figures, namely, the phosphorescent zinc sulphide and the Ba Bi K compound. In all three of these cases it will be noted that the time required for the phosphorescence to fall to a given intensity varies greatly with the temperature and that the curves showing these changes have marked maxima and minima. In the

case of the zinc sulphide, for example, the longest duration observed
was at — 40° but there is evidently another maximum at some
temperature above that of the room and still another at or below
the temperature of liquid air. The curve for Ba Bi K shows a
very pronounced and remarkable maximum at — 132°, above and
below which temperature the duration of phosphorescence falls off
with great rapidity. Between — 40° and — 80° the duration is so
short that measurements can scarcely be made with this apparatus.
In the case of the third compound in question (barium sulphide with
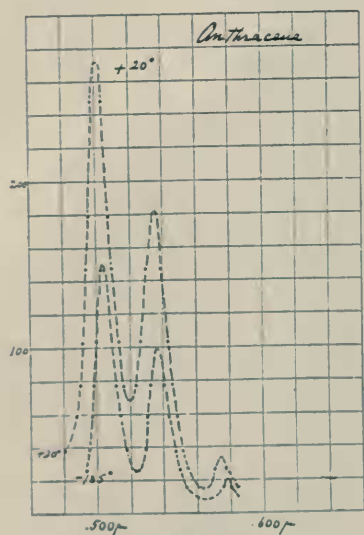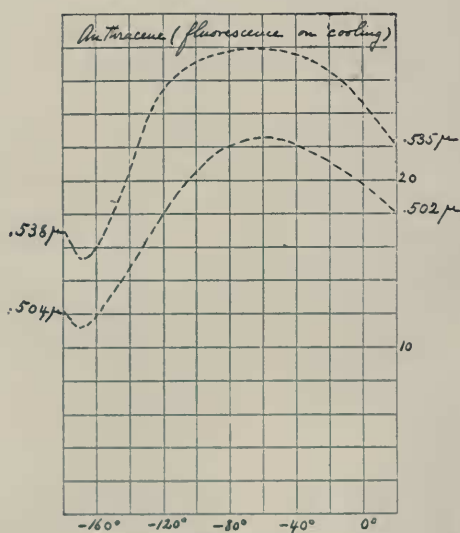

FIG. 10.   FIG. 11.
Fluorescence of solid anthracene.

copper and lithium as the active metals), see Fig. 9, the duration of
phosphorescence falls off as the temperature diminishes until at
about — 60° it is difficult to observe the existence of any phos-
phorescence whatever. The fleeting glow at these temperatures ap-
pears of a different color from that observed either at higher or
lower temperatures. As the temperature of liquid air is approached
the duration increases again until it becomes measurable. It reaches
a maximum at about — 160° after which it begins once more to
decrease.

The study of the fluorescence of these and other substances shows that the relation of fluorescence to phosphorescence is not so simple as at first appears. Observations with the spectrophotometer bring out various complexities in the fluorescence spectrum. Bands that seen with the spectroscope appear to be single are found to consist of two or more components more or less closely overlapping. Changes of temperature affect all wave-lengths of a single band in the same manner and, in some cases, neighboring bands are similarly affected. In the fluorescence spectrum of commercial anthracene for example, there are besides the blue and violet bands of the pure substance, two bright bands having their crests at $.502\,\mu$ and $.538\,\mu$ and a much fainter band with a maximum at $.575\,\mu$. At $-185°$ all three of these bands are reduced in intensity in nearly the same proportion (see Fig. 10). In the case of all three moreover the diminution is greater on the side towards the violet so that there is a slight shift of all three bands towards the red. The positions of the crests are now $.504\,\mu$, $538\,\mu$ and $577\,\mu$ respectively. At the temperature of liquid air moreover the bands are narrower and the yoke between them is much lower.

Observations upon the crests of the two brighter bands, as the substance is gradually cooled, show that the two crests rise and fall in intensity together preserving very nearly the same relative heights as indicated by the curves in Fig. 11.

This displacement of fluorescence bands towards the red on cooling is of frequent occurrence. In the case of the single band in the red-yellow of the fluorescence spectrum of solutions of resorufin in alcohol for instance (see Fig. 12) we find upon reducing the temperature from $+20°$ C. to $-95°$ C. that the intensity at the crest is reduced to about one half and the band is narrower than at room temperature. There is however no appreciable shift. At $-165°$ C. the whole band is shifted to the red and there is further narrowing which shows itself in the steeper slope of the curve on the violet side. The intensity however is the same as at $-95°$ C. Further cooling to $-185°$ C. greatly increases the intensity without further shift. Fig. 13 shows the variations in the brightness of the crest of this band throughout the range from $+20°$ to $-185°$. It

might be thought that since the solvent is alcohol which freezes at
— 112° the shift of the band is due to the change from a liquid to a
solid solution, but this would not account for the changes occurring
in the fluorescence of anthracene nor for the very marked shift
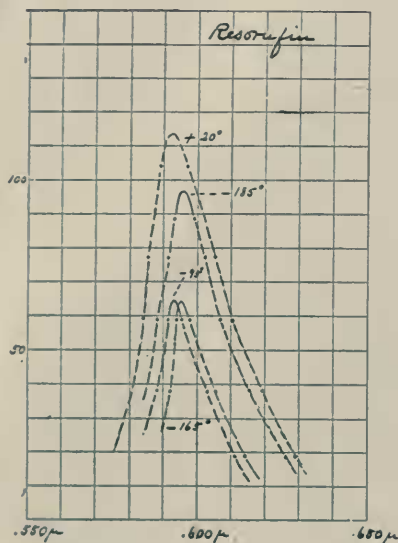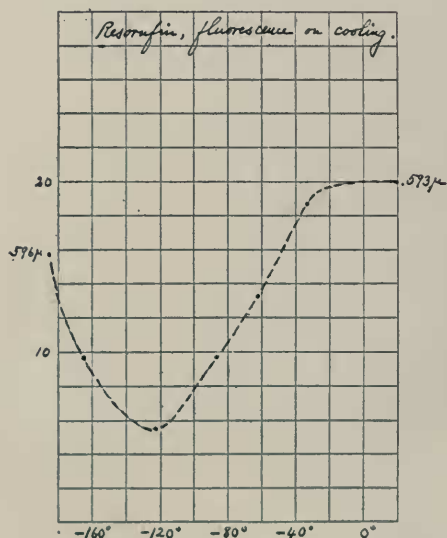towards the red observed in the case of willemite (Fig. 14).

FIG. 12.   FIG. 13.

Fluorescence of resorufin.

In this fluorescent silicate, willemite, the band at + 20° is evi-
dently complex, a closely overlapping band towards the violet being
indicated by the slight notch or shoulder at .51μ (Fig. 14). Upon
cooling to — 70° this component is suppressed and as a result the
violet edge of the band is greatly shifted. Whether the shifting of
the crest, which occurs on further cooling is altogether due to this
cause cannot be definitely determined from these observations.

A very interesting example of a complex band exists in the case
of a phosphorescent sulphide of strontium prepared by the method
of Lenard and Klatt with bismuth as the active metal and a sodium
salt as flux. Measurements of the fluorescence spectrum made with
the spectrophotometer when this substance at + 20° is excited by

the light of the mercury arc, give a curve of the form shown in
Fig. 15.   There is a narrow band with a sharp peak at wave-length.
.494μ and a group of two or more much weaker, over-lapping bands
towards the violet.   At the temperature of liquid air the band
towards the red is reduced in brightness and is shifted towards the
violet, the group of bands of shorter wave-length, however, are
greatly increased in intensity and the curve shows the presence of at
least four crests, at .480μ, .474μ, .468μ and .463μ.
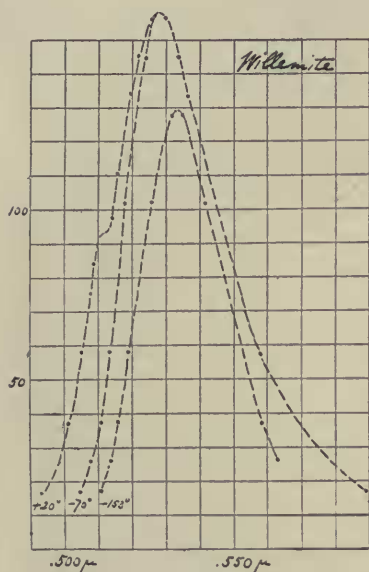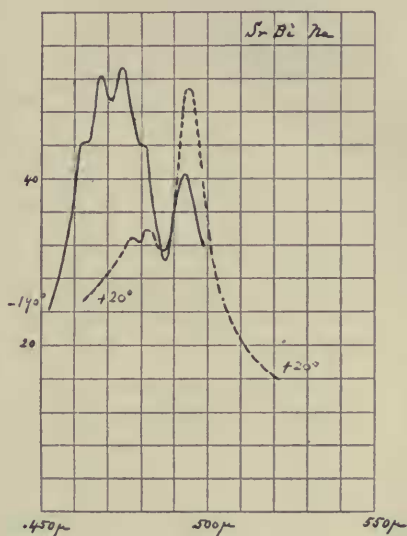

FIG. 14.   FIG. 15.

When viewed in the ordinary way with the spectroscope this
entire group appears as a single broad band and indeed it has been
so designated by Lenard[11] in a recent paper.   When however we
consider that each of its overlapping components is independently
affected, by temperature as to wave-length, intensity and rate of
decay it will be seen that any complete and quantitative study of
the fluorescence and phosphorescence is a very complicated and diffi-
cult matter.

Numerous spectrophotometric measurements, of the spectra of

[11] Lenard, *Ann. der Physik,* IV., Vol. 31, p. 641, 1910.

fluorescent and phosphorescent substances made by Professor Merritt and the present writer, of which a few typical examples have been given in this paper, lead to the following general conclusions.

1. The emission spectra of fluorescent and phosphorescent bodies even when they appear to consist of a single broad band are frequently complex consisting of a group of overlapping bands.

2. The various components of a broad band vary in intensity (both relative and absolute) with the temperature.

3. Sometimes neighboring components of a band are similarly affected by a given change of temperature; sometimes they are oppositely affected, one component increasing in brightness while another diminishes.

4. Change of temperature is frequently accompanied by a shift of the bands of a fluorescence spectrum and this shift, which is sometimes toward the red and sometimes towards the violet, appears in many cases to be due to simultaneous and opposite changes in the intensity of overlapping components.

5. The rate of decay of phosphorescence depends upon the temperature and the complexity of the changes observed when the phosphorescent light is studied as a whole may probably be ascribed the independent variations, as to brightness, duration and position of the various overlapping bands of which the spectrum is composed.

6. Many of the changes in the color of fluorescence and phosphorescence may be ascribed to these independent variations in the intensity and differences in the duration of the overlapping components.

PHYSICS LABORATORY OF CORNELL UNIVERSITY,
April, 1910.